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Enhancing the hydrophobic properties of various commercial polymers through mixtures and coatings with a fluorinated diblock copolymer in low concentrations



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ABSTRACT

In this work the ability of a fluoro-modified copolymer (SBF) derived from a chemically modified PS-*b*-PB_{1,2} [PS: polystyrene and PB_{1,2}: poly(butadiene) with exclusively 100% 1,2-microstructure] is evaluated, since the fluoro-modified copolymer (SBF) showed enhanced hydrophobicity when compared with the neat diblock. The stiff fluoro-ligand of the side group leads to different chemical and physical properties, which characterized by various techniques. From contact angle measurements the SBF modified copolymer exhibited high contact angle (113.6°) and low surface energy (6.54 mN/m), which were increased further through thermal treatment, due to the orientation of the ligands. Additionally SBF used in mixtures and coatings in low concentration (maximum up to 2wt% for the PB segment in respect to the total mass) with commercial polymers in order, again, to evaluate the hydrophobic properties. For this purpose various copolymers such as the initial diblock precursor (SB_{1,2}), commercially available triblock copolymer of the SBS type and a hydrophilic commercial homopolymer of poly(ethylene glycol) (PEG) were chosen. It was found that both contact angle and surface energy were improved significantly in all cases despite the very low amount of the SBF component in the final system for all mixtures and/or coatings.

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1. Introduction

Fluoropolymers are considered an important class of polymeric materials. Numerous monomers which can be modified with fluoro-derivatives bearing fluorine (F) atoms in their main chain or as a side group can be synthesized leading to this specific polymer group. Various architectures of such materials have been reported in the literature [1]: e.g. homopolymers, copolymers, crosslinked and multiblock copolymers. Three different procedures to incorporate fluorine (F) atoms in polymeric materials have been proposed: (i) polymerization of a monomer with F atoms

in the main chain, (ii) modification of a polymer in the end groups with fluoro-derivatives and (iii) modification of a side group [1]. The reason for using these polymers is related to their unique properties, and especially due to their low surface energy. The location of -F- atoms or moieties (-CF₃ or -CF₂-) on the surface of specific matrices converts them to hydrophobic exhibiting contact angles higher than 90° [2].

The low surface energy of fluoropolymers makes them attractive for many applications [3–10]. The existence of a linear flexible backbone becomes crucial in order to create hydrophobic surfaces [11]. It has been reported that fluorinated materials with relatively high contact angles can be prepared by mixing polymers with fluoropolymers obtaining contact angle values as high as 122° [12].

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Besides hydrophobicity, fluoropolymers have many other interesting properties, such as chemical inertness [3,12], thermal stability, low refractive index, low relative permeability, lipophobicity, low friction coefficient [4,12] as well as weather and aging resistance. Due to these unique properties, many applications such as coatings [4], tribologically active coatings [13], microelectronics [14], antifouling [15], antiwetting, optics, biomaterials, lubricants, surfactants, aerospace, lithography and sensors [4,9,14–16] have been reported. In order to achieve such applications fluoropolymers with different chemical structures, architectures and various methods of polymerization (or modification) can be developed. One of the approaches is the use of polystyrene (PS) based block copolymers with fluorinated aromatic substituents in the side groups [4] or another approach which involve the use of fluorinated methacrylates [7]. Plasma polymerization has also been reported leading to perfluoroacrylates (with critical surface tension $\gamma_c = 4.3$ mN/m) [16] as well as to semifluorinated single side groups attached to a polyisoprene homopolymer [17].

Furthermore, poly(acrylic acid)-*b*-PS copolymer to poly(ethoxylatedfluoroalkyl acrylate)-*b*-PS [18] and diblock copolymer PS-*b*-PB_{1,2} (where PS polystyrene and PB_{1,2} polybutadiene with approximately 100% 1,2-microstructure) copolymer with pentadecafluorooctanoyl chloride [19] have been reported. The latter precursor (PS-*b*-PB_{1,2}) is the copolymer used in this research study [19], as shown in Fig. 1. Materials combining properties of both fluoropolymers and polysiloxanes (both materials are known for their hydrophobic character) should also be mentioned. Some examples are poly(dimethylsiloxane)-*b*-P(2,2,3,3,4,4,4-heptafluorobutyl methacrylate) prepared by ATRP [9] and PS-*b*-PI_{3,4/1,2} modified with short perfluoroalkyl or dimethyl siloxy groups [20].

The ability of these materials to exhibit low surface energy and therefore be ideal for hydrophobic surfaces is affected by the orientation of the side groups in the surface (air–polymer interface). Mesophase polymers can present properties linked to their amorphous glassy, elastic or three dimensionally ordered crystalline structures [21]. Side chains containing different groups such as $-\text{CH}_2-$, $-\text{CH}_3$, $-\text{CF}_2-$ and $-\text{CF}_3$ are responsible for the orientation of such groups in the material surface, thus affecting the total surface energy. Another important factor is the molecular weight of the polymer or copolymer which can enhance the side mesogenic groups to differentiate from the main backbone [15]. The length and the chemical components (e.g. $-\text{CH}_2-$ and $-\text{CF}_2-$) of the side group are crucial for achieving low surface energy materials. It has

been reported that surfaces with longer side chains and more fluorine atoms than hydrogen may lead to lower surface energy materials [4,10,14,15,22]. Orientation of $-\text{CF}_3$ without the orientation of $-\text{CH}_2-$, $-\text{CH}_3$ or $-\text{CF}_2-$ in the outermost surface exhibits desirable results for low surface energy materials. These groups ($-\text{CF}_3$) can be arranged on the surface in a hexagonally organized layer where longer side chains can form the hexagonally close packed arrays of $-\text{CF}_3$ [10]. One important drawback is the problematic adhesion onto surfaces, which leads eventually to the reconstruction of their structure. Such behavior (reconstruction) can be avoided by the ideal separation of side chains since longer side chains lead to immiscibility with the polymer backbone. The separation is much more successful when the surface consists mainly of $-\text{CF}_3$ groups and not a mixture of $-\text{CH}_2-$, $-\text{CH}_3$ or $-\text{CF}_2-$ groups [10]. Thermal treatment is also a useful tool for avoiding such behavior leading eventually to reconstruction of the surface [7,22].

In this manuscript we initially describe the evaluation of the surface properties by changing temperature of a precursor diblock copolymer of the PS-*b*-PB_{1,2} type modified with pentadecafluorooctanoyl chloride (abbreviation which will be used throughout the manuscript is SB_{1,2} for the initial and SBF for the modified diblock copolymer) and secondly the use of small amount of this fluoropolymer (maximum 10 wt% and 2% for the PB fluorinated segment in respect to the total mass) with commercial polymers (such as PS-*b*-PB-*b*-PS and PEG) in order to enhance their hydrophobic properties. The use of hydrophobic materials in mixtures with commercial polymers in low concentrations is a field that has not fully evaluated and exist a need for investigation.

Results concerning hydrophobicity and surface energy have been obtained through contact angle measurements. The diblock copolymer involves PS segments in order to increase the adhesion onto the surface and the solubility in various organic solvents [19]. The results are divided into two sections: initially the microstructure and surface properties of the modified SBF copolymer are analyzed and secondly the hydrophobic properties of the initial precursor SB_{1,2}, a commercial PS-*b*-PB-*b*-PS (referred as SBS), as well as those of their mixtures and coatings with SBF, also including PEG/SBF [PEG: poly(ethylene glycol), a hydrophilic polymer] are investigated.

2. Experimental

2.1. Materials

Four different polymers were used: one homopolymer and three copolymers. PS-*b*-PB_{1,2} (approximately 100% 1,2-microstructure for the PB segments) was synthesized via anionic polymerization and modified with pentadecafluorooctanoyl chloride, in order to achieve a fluorinated material with pendant fluorine side chains in the PB block. It should be pointed that the substitution degree of the PB block from the pentadecafluorooctanoyl chloride was almost 100% as already reported in the literature [19], where the synthesis of the aforementioned copolymer, details

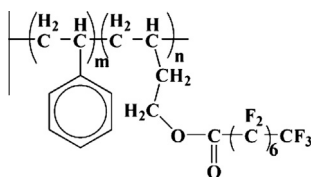


Fig. 1. Schematic of the chemical structure for the modified diblock copolymer noted as SBF.

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